

APPLICATION FOR UNITED STATES PATENT

ATMOSPHERIC EQUIVALENT TEMPERATURE ANALYSIS

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CROSS REFERENCE TO RELATED APPLICATION:

This application claims the benefit of U.S. Provisional application 60/258,900 filed December 15, 2000

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CASE NO. CJB-0109



27810

PATENT TRADEMARK OFFICE

ATMOSPHERIC EQUIVALENT TEMPERATURE ANALYSIS

**[0001]** This application relies for priority on provisional application 60/258,900 filed December 15, 2000.

BACKGROUND

**[0002]** The amount and chemical nature of the asphaltic fractions of crude oil of petroleum origin, boiling higher than a selected high temperature (i.e., a typical vacuum distillation cut temperature such as 565°C), are extremely important in the assessment of crude oils. Cuts above 565°C are called vacuum resids. A high residuum content (weight percent yield > 20-30%) indicates a heavy crude with smaller proportion of volatile components, favoring asphalt production. Heteroatomic components predominantly concentrated in the heavier crude fractions can indicate excellent potential to produce premium straight-run asphalt products.

**[0003]** Crude residuum/asphalt quality assessment requires long and tedious physical distillation by conventional methods (e.g., ASTM D2892 and ASTM D5236). Conventional distillation methods require a minimum of two days to recover sufficient residuum sample and a whole crude sample of at least 4 liters depending on asphalt yield and the number of asphalt tests required after distillation. Though generally not used for asphalt, thermal gravimetric analysis (TGA) can use small samples, generally uses atmospheric pressure and maybe low vacuums resulting in long sample analysis, and is only repeatable within 2-3% error. It would be beneficial to use small samples (e.g., 5 ml) of whole crude that could be quickly and safely transported for rapid analysis.

## SUMMARY

[0004] This method generates asphalt/residuum from very small volumes of whole crude, a feature not possible with current conventional distillation methods. The new method is based on the exposure of crude to accurately controlled temperature and vacuum conditions. The asphalt/residuum is obtained as the residual material remaining after vaporization of the lighter crude components. The weight percent of residuum (asphalt fraction) in the crude is determined by mass balance (i.e., see Figure 1).

## BRIEF DESCRIPTION OF THE DRAWINGS

[0005] Figure 1 shows a basic schematic of a preferred embodiment.

[0006] Figure 2 shows a basic flowchart of a preferred embodiment.

[0007] Figure 3 shows a basic schematic of the heated vacuum chamber.

[0008] Figure 4 shows representative yields versus temperature derived by the invention.

[0009] Figure 5 compares the invention to various other tests.

[0010] Figure 6 shows a mass spectrometry comparison.

## DETAILED DESCRIPTION

[0011] Residuum remains from distilling crude and is often used at least in part for asphalt. The present invention allows very quick production of very small samples of residuum with minimal thermal degradation. Main advantages for this method over previous methods (conventional distillation techniques) are:

(a) shorter time (e.g., 20-30 minutes versus 1-2 days), (b) smaller sample size (e.g., 5 ml versus 4000 ml), (c) repeatability, (d) adaptable to determine yields at other temperatures, (e) less liable to thermal cracking than with conventional distillation techniques at extreme temperatures.

[0012] This method permits the preparation and collection of the asphaltic fraction or vacuum residuum from a crude oil at a selected AEBP (atmospheric equivalent boiling point) in a short period of time (e.g., 20-30 minutes) from a small sample volume (e.g., 5 ml whole crude). The weight percent yield of asphalt /residuum can be determined from the mass balance to an accuracy of 2 wt%. Sample preparation is accomplished using an apparatus which can accurately heat the whole crude at a selected temperature for a given period of time at constant low pressure. It is important that the apparatus demonstrates excellent long-term stability for both temperature and vacuum conditions. The temperature and vacuum of the apparatus may be variable although once the temperature corresponding to the target AET at a given pressure has been established, then both temperature and pressure are maintained constant throughout the experiment. Incorporation of sub-ambient (vacuum) pressure in the experiment prevents thermal cracking of the asphalt/residuum. To obtain the asphalt/residuum, it is necessary to determine the exact temperature-pressure combination which corresponds to the target AET. This can be done as outlined in ASTM D5236 however that procedure requires accurate measurement of both temperature and pressure. It is simple to measure the temperature of the apparatus during this procedure however it is generally difficult to measure the working pressure. To avoid direct measurement of pressure, this method uses the distillation profiles of a set of known crudes to calibrate the apparatus for temperature-pressure conditions. Correlation of process temperature readout to AET is determined using the calibrant crudes distillation profiles. The overall procedure is outlined in Figure 2.

[0013] The preferred method is to place a weighed frozen crude sample in a small closed chamber, that is then roughly pumped down by a mechanical pump, and then opening a passage from the small closed chamber to a chamber with at least 1 L volume (i.e., heated manifold) at a know vacuum level (e.g., 1 milliTorr). Intermediate products, resids, and aged asphalt can be used instead of or mixed with the crude. Preferred samples sizes are 10-40 mg, though 2-200 mg are envisioned as part of this invention. The resid remaining after equilibrium is then taken out and reweighed. The ratio of the first weighing to the second weighing gives the AET yield. Other information can be determined from analyzing gases from the vacuum pump line or the vacuum chamber depending on whether the vacuum chamber is continuously pumped down or closed off after reaching the required pressure and then exposed to the sample. The remaining resid could also be analyzed. The calibration part of this invention could also be used to calibrate thermal or microthermal analysis techniques.

[0014] A block diagram of the apparatus used for the new method is presented in Figure 3. The preferred apparatus has a sample oven (A), a sample holder (B), and an all-glass heated manifold (C). The apparatus is capable of achieving 1 milliTorr ( $10^{-3}$  Torr) absolute pressure. The sample is weighed into a quartz tube boat and cooled in a liquid nitrogen bath. It is then placed in sample holder (B) and attached to manifold (C). High temperature glass valves in the manifold are used to expose the sample to sub-ambient pressure. Other boats may be used, though quartz is preferred. On exposure of the sample to vacuum pressure, the sample oven is heated from ambient to target temperature and maintained at that temperature for a selected time period. The manifold, which is maintained at constant high temperature (300-350°C) throughout sample preparation, permits a physical interface between the sample holder and the vacuum pressure generated by the apparatus. In this manner, it is not

necessary to develop and disperse vacuum pressure for each crude to be reduced. This greatly decreases sample preparation time for asphalt/residuum from whole crude. Approximately 20 g of asphalt or residuum is produced from 5 ml of whole crude by this method, depending on AEBP and the nature of the crude.

**[0015]** Figure 4 illustrates the calibration approach using a set of three very different crudes: Murban, Arab Light, and Arab Heavy. The weight percent yield determined by mass balance is plotted as a function of process temperature. The whole crude sample was held at target temperature for 15 minutes under constant vacuum pressure. The process temperature under vacuum conditions, which corresponds to an AET of 565°C, was determined by equivalent yields. For the pressure conditions selected in the new method, a process temperature of 225°C for 15 minutes produced a 565°C + equivalent asphalt/residuum.

**[0016]** Quality control weight percent yield data for Murban crude at 565°C over a four-month period gave 565°C AET yields of 90.31, 90.12, 90.36, 90.38, 90.56, 90.02, 90.46, 90.12, 90.57, 90.25, 90.10, 90.36, 90.13, 90.45, 89.99, 90.10, 90.01, 90.15, 90.15, 90.41, 90.23, and 90.09. The average weight percent yield was 90.24%, with a standard deviation of 0.18%. Method weight percent yields are compared to distillation weight percent yields for crudes at 565°C AET in Table 1. The largest difference in yields generated by the two methods is less than 2%. These results confirm the repeatability and accuracy of the new method, based on conventional distillation results.

Table 1

Crude Sample	Measured Yield (wt% @ 565°C AET)		Measured Average Yield	Known Yield (wt% @ 565°C)	Difference
	Run #1	Run #2			
1	67.24	66.65	66.95	68.03	-1.09
2	67.60	67.72	67.66	67.91	-0.25
3	74.41	74.34	74.38	73.60	+0.78

[0017] Asphalts and residua prepared from the same crude slates by the new method and by conventional distillation were compared using UV analysis (800 ppm asphalt in tetrahydrofuran). The results for the COLDLK96 and URNOVO96 samples in Figure 5 confirm the molecular equivalence of asphalts produced by these methods. Similar UV results were obtained with other sets of crudes.

[0018] Figure 6 compares residua from Mandji crude prepared by the new method and by conventional distillation using Pyrolysis GC/MS. The Pyrolysis GC/MS method thermally degrades asphalt/residuum by exposure to high temperature (approx. 650°C). The volatile pyrolysis products are analyzed by GC/MS. The total ion current traces in the chromatograms demonstrate excellent similarity between residua prepared by the two methods. An accumulated mass spectrum was obtained by integration of all mass spectra in the Pyrolysis GC/MS runs. The hydrocarbon compound types found in the residua produced by the new method and by conventional distillation confirm that the new method generates residua which are almost identical to those obtained by conventional distillation. Similar correlation was demonstrated by Pyrolysis GC/MS for several other crude slates.

[0019] The method of the present invention permits rapid evaluation of the asphalt potential for a crude by producing an asphalt specimen which is suitable for further analytical evaluation within 20-30 minutes and by indicating weight percent yield (2% at 565°C+) or process AET (Atmospheric Equivalent Temperature) from mass balance. Equivalent physical distillation requires approximately 48 hours on the stills.

[0020] The method of the present invention requires a very small volume of whole crude. A 5 ml representative sample is sufficient to perform several runs. The sample holder is charged with 1-20 mg. Conventional distillation requires a minimum of 4 liters of whole crude for evaluation of potential asphalt quality, depending on the specification tests required and the yield of the particular crude slate.

[0021] The method of the present invention demonstrates excellent repeatability. In addition to asphalt/residuum preparation to evaluate asphalt potential and yield, it can be used to monitor crude quality changes, the presence of pipeline contamination, or co-mingling and estimate their effects on asphalt quality and yield.

[0022] The method of the present invention can be modified to obtain the weight percent (wt%) yield and to generate asphalt/residuum specimens at AET other than 565°C of interest to specific refinery and plant operations or research needs. The new method is particularly useful where crudes have been contaminated by unknown components with overall adverse effect of not being able to meet product specifications. The new method can rapidly identify the presence of contamination through yield changes and can produce a sample suitable for the further application of advanced analytic techniques. The yield can be compared to a standard for that crude to determine a pass/no pass decision tree.

[0023] The method of the present invention is suited to determine the potential asphalt content of crudes which are subject to thermal cracking under conventional distillation conditions, due to low-pressure conditions. Heavy asphaltic crudes, which produce premium straight run asphalt products, tend to crack within the temperature range of conventional distillation methods. Multiple runs with the new method varying either residence time at high temperature or process temperature itself can generate a yield profile for an unknown crude in a short time frame (e.g., 30 minutes/run).

[0024] The method of the present invention can be used to generate asphalt/residua samples which are suitable for further analysis by other analytical methods such as GC, HPLC, MS, HR MS, and others. This is a significant advantage in the timely evaluation of asphalt potential for new or unknown crudes, crude blends, and spot market opportunities.

[0025] The method of the present invention is different from plant vacuum distillation by using higher vacuum than used by plant processes ( $> 10^{-3}$  Torr), rapid exposure of a sealed sample to vacuum, and use of much smaller volumes that give much faster equilibrium times.

[0026] Preferred sample formats are sheets, thin films, and drops. These sample forms allow for a high enough surface area to rapidly cool or heat the sample. A higher vacuum (lower pressure) in the oven allows a lower oven temperature and therefore less sample degradation. The preferred mode of this invention uses fixed temperature ovens with sample equilibration time of less than or equal to 15 minutes, a constant vacuum buffer, and a 0.2% repeatability. The term "freezing" means cooling to a temperature low enough such that water does not vaporize enough in at least 30-60 seconds to cause sample damage.